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NATURAL DYE FROM THE BARK OF *CASUARINA EQUISETIFOLIA* FOR SILK

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ABSTRACT

The use of natural dyes as an alternative to synthetic dyes has attracted increasing attention in view of hazards and environmental pollution caused by synthetic dyes and pigments. Natural dye was extracted from *Casuarina equisetifolia* bark, which hitherto was treated as waste material. The dye uptake and fixation as well as the influence of mordants on the colorimetric and fastness properties have been demonstrated. K/S values of the dyed fabrics were also evaluated and the effect of mordant type with different mordanting methods on dyeing was studied. The extracted dye was tested against gram-positive and gram-negative bacteria for antimicrobial activity. The eco-friendliness of the dye was verified by analyzing the metal content, pesticides and amines. The mordant dyed samples showed improved colour values and fastness properties besides exhibiting antibacterial property indicating its potential for use in the textile industry.

KEYWORDS: ***Casuarina equisetifolia,*** **Dyeing, Mordant, Silk, Toxicity**

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INTRODUCTION

Natural dyes have been extensively used since ancient times for textile coloring[1]. The dyes extracted from natural sources were less competitive and were therefore gradually replaced by synthetic dyes. But nowadays, extraction and application of natural dyes are becoming more popular owing to the growing awareness of environmental problems coupled with the toxicity associated with synthetic dyes[2,3]. As a result, renewable resources are now being reinvestigated as potential alternative raw materials[4,5]. Various national and international organizations are engaged in extracting colors for dyeing from natural sources and efforts are still being made by researchers to overcome various drawbacks of natural dyes such as availability, poor reproducibility and lack of desirable fastness properties on textiles. Furthermore, natural dyes are known to exhibit better biodegradability, less toxicity, eco-friendly alternatives to synthetic dyes[6] and some dyes also possess medicinal properties[7,8].

Casuarina equisetifolia is an evergreen tree of Australia origin[9], extending to islands of the Pacific and to Southeast Asia. Due to its multiple utility and adaptability to different eco-climatic and edaphic zones of the country, this species has gained importance in the forestation of coastal areas, degraded and eroded sites, where soil nutrients are scarce. Since the tree has a short rotation period, it is also preferred as an agro-forestry crop, and mainly grown for its fuel wood particularly in Karnataka and Tamilnadu states of India[10,11]. The major chemical constituents are ellagic acid, gallic acid, kaemferol and quercetin[12] and the bark contains astringent and antioxidant properties[13] and also has significant anticancer and anthelmintic potential[14,15]. In the present work, an attempt has been made to extract the dye from the bark of *Casuarina equisetifolia* for dyeing silk using different mordants.

MATERIALS AND METHODS

Raw material

The bark of the *Casuarina equisetifolia* (Fig. 5) was collected from the agriculture field at Malur, Kolar district (Karnataka) and dried at room temperature.

(i) Extraction of the dye

Casuarina equisetifolia bark was chopped into small chips which were then boiled in water for 45 min, using MLR of 1:40 to get an aqueous colored solution.

(ii) Dyeing silk fabrics

Plain woven degummed mulberry silk fabric weighing 40 g/m^2 with a yarn density of 132 ends/inch and 116 picks/inch was selected for dyeing. The dyeing was carried out at 90^{o}C with the dye bath pH 5 containing 10 % dye (owf) at MLR 1:20 in a temperature controlled beaker dyeing machine for 60 min. The dyed samples were subsequently washed in 1 gpl non-ionic detergent solution at 60^{o}C for 15 min and dried at room temperature.

(iii) Absorbance and Color Strength Measurements

Dye solutions (1-5%) were prepared from the crude extract by maintaining material-to-liquor (MLR) ratio at 1:20. The absorbance of the dye solution was recorded before and after dyeing process with UV-Visible spectrophotometer. The per cent dye uptake was calculated using the following formula

$$\%\ Dye\ uptake = \frac{Absorbance\ before\ dyeing - Absorbance\ after\ dyeing}{Absorbance\ before\ dyeing} \times 100 \quad ……(1)$$

(iv) Mordanting
The substrates were pre-and post-mordanted using 2 % and 5 % (owf) solutions of each of potassium aluminum sulphate, tannic acid and tartaric acid separately with MLR 1:20 for 30 min at 60°C. The fabrics were subsequently rinsed and dried.

(v) Measurement of surface color strength and color value
Color was evaluated by means of K/S and CIELAB values with illuminant $D_{65}/10^{\circ}$ observer on Gretag Macbeth Color Eye 7000 A Spectrophotometer. Four measurements were made for each sample and the variation in percentage reflectance values over a range of 350–750 nm was recorded. The K/S values were assessed using the Kubelka-Munk equation.

$$K/S= (1-R)^2/2R \quad \text{....(2)}$$

Where, R is the observed reflectance, K is the absorption co-efficient and S is the light scattering co-efficient.

(vi) Dye exhaustion and fixation
The extent of dye exhaustion was determined spectrophotometrically, wherein the absorbance of dye bath solution before and after the dyeing process was recorded at the λ_{max} of the dye. The percentage dye exhaustion (%*E*) was calculated using equation (3)[16], where A_0 and A_1 are the absorbance of the dye bath before and after dyeing, respectively.

$$\%E=[(A_0-A_1)/A_0]\times 100\% \quad \text{....(3)}$$

The total fixation efficiency (*T*), which is the percentage of the fixed dye, was calculated using equation (4) [16].

$$\%T=[(A_0-A_1-A_2)/A_0]\times 100\% \quad \text{.... (4)}$$

where A_0, A_1, and A_2 are the respective absorbance values of the dye before dyeing (A_0), after dyeing (A_1), and in the wash-off solution after stripping with DMF (A_1) respectively. From the dye exhaustion and the total fixation efficiency values, the fixation values of the dye absorbed (*F*), sometimes termed the fixation ratio, were calculated using equation (5)[16].

$$\%F=\%T/\%E \quad \text{.... (5)}$$

(vii) Measurement of fastness properties
Color fastness to light (IS 2454: 1985), washing (ISO: 105:102) and crocking (ISO: 105:E04) was carried out in a Fad-o-meter, Launderometer and Crockmeter respectively as per ISO standard methods.

(viii) Elemental Analysis
Heavy metal concentrations in the digested samples were determined with A6300 Shimadzu flame atomic absorption spectrophotometer with Shimadzu auto sampler (Asc-600). The calibration curves were prepared separately for all the metals by running different concentrations of standard solutions[17]. The extracted dye was also analyzed for the presence of banned aryl amines after reductive cleavage and isolation using GC/MS.

(ix) Antimicrobial activity

Escherichia coli (E. coli) a gram-negative bacterium, was selected due to its popularity of being a chosen test organism and its resistance to common antimicrobial agents, *Staphylococcus aureus (S. aureus)*, a pathogenic gram-positive bacterium was used because it was the major cause of cross-infection in hospitals and it is the most frequently evaluated species[18,19]. 1g silk fabric (dyed and undyed seperately) was introduced into the 100 ml nutrient broth inoculated with the microbes and incubated at 37^{o}C for 16 h. The reduction of bacterial growth by the dye was expressed as follows:

$$R=100(A-B)/A \quad \text{.... (6)}$$

where *R*= % reduction in bacterial population; *A*=absorbance (660 nm) of the media inoculated with bacteria and undyed fabric; *B*= absorbance (660 nm) of the media with bacteria and dyed fabric[20].

RESULTS AND DISCUSSION

1. Effect of Dyeing conditions

Fig. 6 shows that the pH values of the dye bath have a considerable effect on the dye-ability of silk fabric. As the pH increases, the dye-ability decreases, the effect of the dye bath pH can be attributed to the correlation between dye and silk fibers. Since the dye used is a water soluble dye containing anionic groups it would interact ionically with the protonated terminal amino groups of silk fibers at acidic pH via ion exchange reaction. This ionic attraction would increase the dye ability of the fiber as clearly observed in Fig. 6. The decrease in dyeability at pH higher than 3 may be attributed to the enhanced desorption of the dye[21]. The effect of dyeing time on color strength is shown in Fig 7. Longer dyeing time means higher color strength until dye exhaustion attains equilibrium and there is no significant increase after further increase in dyeing time. The decrease in color strength for 120 minutes of dyeing may be attributed to desorption of the dye molecules as a consequence of over dyeing[22].

2. Effect of Dye concentration on dyeing

Within the range of dye concentration studied (0.5-15%), the maximum uptake was observed at 10 % of the dye concentration (Table 1). Further, K/S values also increased with the increase in dye concentration indicating deeper shades. The maximum dye concentration of 10% was therefore taken for further dyeing process.

3. Effect of mordants on color strength

It is clear that the type of mordants has influence on the color strength, fixation ratio, hue as well as the fastness to wash and light by forming additional linkage with dye molecules compared to the silk samples dyed without any mordant[23]. This can be determined by the increase in the dye exhaustion and fixation as shown in Figs 8, 9, 10 and 11 as well as the colorimetric analysis and fastness to wash and light shown in Table 3. It is evident that the highest values of color strength and fixation, as well as fastness to wash and light were achieved with mordants. Table 2 shows the K/S values and CIELAB co-ordinates L, a*, b*, C and h of silk fabric dyed with *Casuarina equisetifolia* bark. It is observed that the K/S values of the dyed material using different mordants (alum, tannic acid and tartaric acid) increased as compared to the control sample. The K/S values were highest in the case of dyed samples mordanted with alum and tannic acid (pre mordanting technique) and tartaric acid (post mordanting technique). Similarly the L values of the dyed samples decreased with the increase in mordant concentration indicating deeper shades as compared to control sample. In all mordanting techniques change in a* and b* values were noticed. The values were also positive for all mordanted samples. Color hues (tone) were redder or yellower.

4. Fastness properties

The fastness ratings of silk fabric dyed with or without mordants are presented in Table 3. The control sample exhibited poor fastness properties and mordanted samples showed improved fastness properties with reference to light, washing, rubbing and perspiration. The reason attributed is tannin content of the dye, which may help in fixation of the dye with the fiber. Hence mordanting alter the light sorption characteristic of tannin as well as make them insoluble in water and ultimately improves washing fastness properties.

5. Antimicrobial activity of Casuarina equisetifolia dye on substrate

It was important to study the antimicrobial activity on dyed textile substrate (silk fabric) because the natural dyes showed inhibition effect against test bacteria in solution. The results are shown in Fig 12. A reduction of 45% and 58% is seen in *E. coli* and *S. aureus* respectively. The antimicrobial activity might be attributed to ellagic acid and tannin components[24,25].

6. Heavy metal content

Table 5 show the extremely low quantities of heavy metals extracted from *Casuarina equisetifolia* bark. As the concentrations are much below the stipulated limits the extracted dye can be considred eco-friendly.

Table 1
Absorbance, dye uptake and colour strength of different dye concentrations of Casuarina equisetifolia bark extract

Dye conc. %	Absorbance		Dye uptake	K/S
	Before dyeing	After dyeing		
0.5	0.12	0.04	33	0.98
1	0.24	0.15	62	1.15
5	0.44	0.35	79	1.67
10	0.86	0.78	90	3.95
15	0.91	0.79	86	3.86

Table 2
K/S and color co-ordinates of silk samples dyed with Casuarina equisetifolia bark extract

Sl No	Mordants	Mordanting Method	Mordant %	K/S	L	a*	b*	C	h
Unmordanted				3.90	51.21	09.80	7.02	56.41	67.06
01	Alum	Pre	2	6.61	46.50	11.02	5.78	57.92	59.75
02			5	6.78	45.72	11.94	5.61	57.65	57.98
03		Post	2	4.95	46.25	11.09	3.95	57.48	62.41
04			5	5.48	45.62	11.21	4.48	58.15	63.64
05	Tannic acid	Pre	2	6.36	48.01	12.67	5.06	58.93	57.26
06			5	6.46	46.95	11.02	5.36	58.66	58.09
07		Post	2	7.07	44.18	12.64	6.07	57.71	57.58
08			5	7.28	43.49	12.41	6.28	58.57	57.96
09	Tartaric acid	Pre	2	4.29	48.99	9.92	3.29	58.65	56.51
10			5	4.30	47.28	9.83	3.26	55.12	57.34
11		Post	2	5.36	48.11	10.97	4.36	55.42	57.68
12			5	6.29	48.06	10.79	5.29	55.91	58.75

Table 3
Fastness properties of silk samples dyed with Casuarina equisetifolia bark extract

Sl no	Mordants	Mordanting Method	Mordant %	Light Fastness	Wash fastness		Perspiration fastness				Rubbing fastness	
							Acidic		Alkali		Wet	Dry
					CC	CS	CC	CS	CC	CS		
Unmordanted				2	2	5	2-3	5	2	5	3	4
01	Alum	Pre	2	2-3	3	5	3	5	3	5	3-4	4-5
02			5	2-3	3-4	5	3	5	3	5	3-4	4-5
03		Post	2	2	3-4	5	3	5	3	5	4	5
04			5	2-3	4	5	3	5	3	5	3-4	4
05	Tannic acid	Pre	2	2	3-4	5	3	5	3	5	3-4	3-4
06			5	2	4	5	3	5	3	5	3-4	3-4
07		Post	2	2	3	5	3	5	3	5	3	4
08			5	2-3	3	5	3	5	3	5	3	4
09	Tartaric acid	Pre	2	2	3-4	5	3	5	3	5	4	5
10			5	2	3	5	3	5	3	5	4-5	5
11		Post	2	2-3	4	5	3	5	3	5	4	5
12			5	2-3	4	5	3	5	3	5	4	5

Table 4
Concentration of red listed chemicals in the extracted dye

Sl No	Heavy metals	Permissible range (ppm)	*Dye* (ppm)
1	Arsenic	0.001-0.01	0.01
2	Cadmium	0.0005-0.005	0.002
3	Chromium	0.01-20	Ab
4	Cobalt	0.02-20	0.08
5	Copper	0.3-100	Ab
6	Lead	0.004-0.04	0.001
7	Mercury	0.0001-0.1	Ab
8	Nickel	0.02-10	0.07
9	Zinc	0.5-5.0	0.29
10	Pesticides	----	NT
11	Banned aryl amines	----	NT

NT: Not traceable, Ab: Absent, ppm: Parts per million

Figure 1
Ellagic Acid

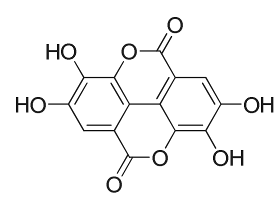


Figure 2
Quercetin

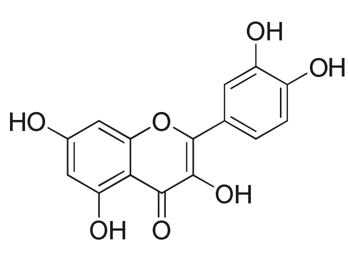


Figure 3
Gallic acid

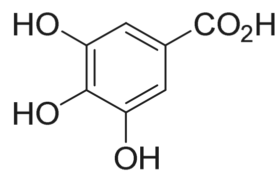


Figure 4
Kaemferol

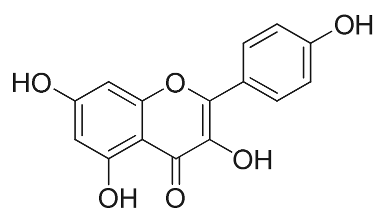


Figure 5
Casuarinaequisetifolia (Insect-stem bark)

Figure 6
Effect of dye bath pH on Colour strength of silk

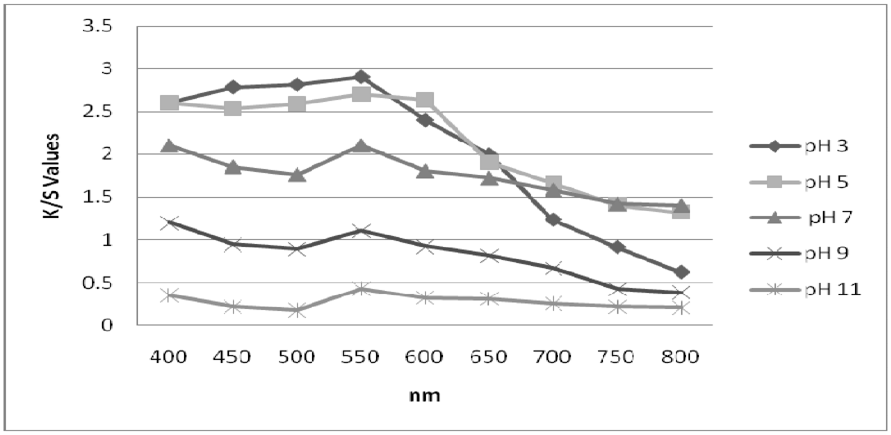


Figure 7
Effect of dyeing duration on colour strength

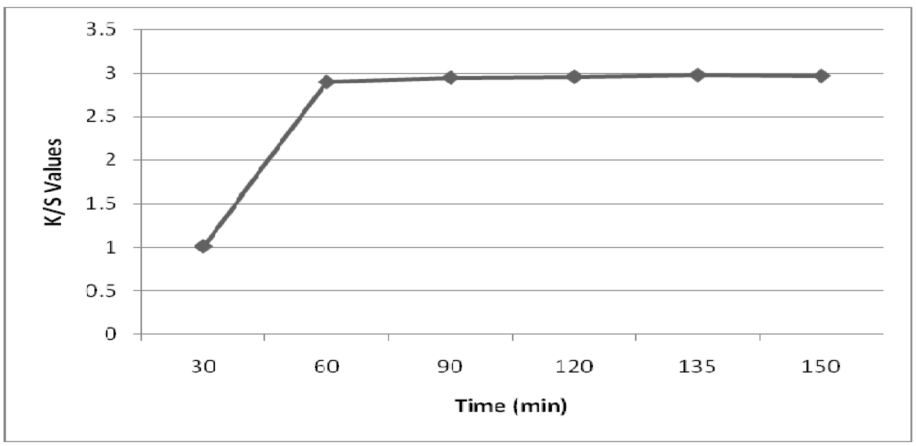


Figure 8
Effect of dyeing time on the percentage dye bath exhaustion (%E)

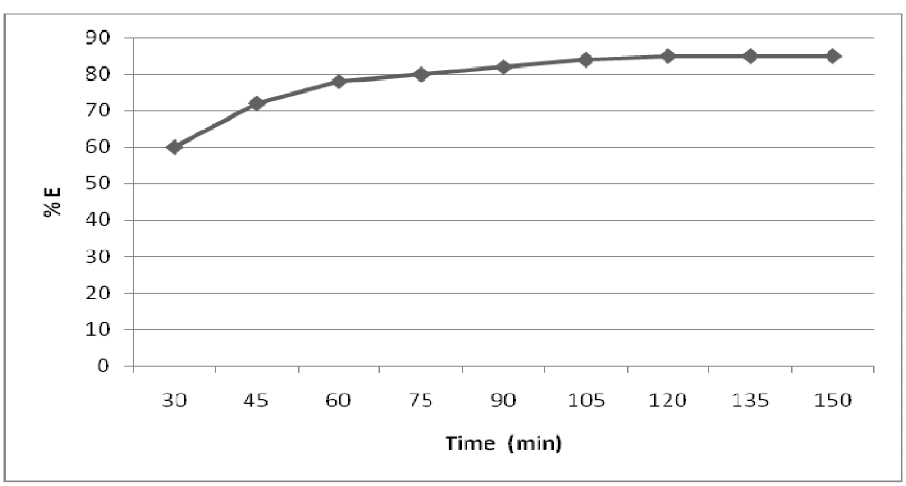


Figure 9
Effect of mordants on the percentage of dye exhaustion (%E)

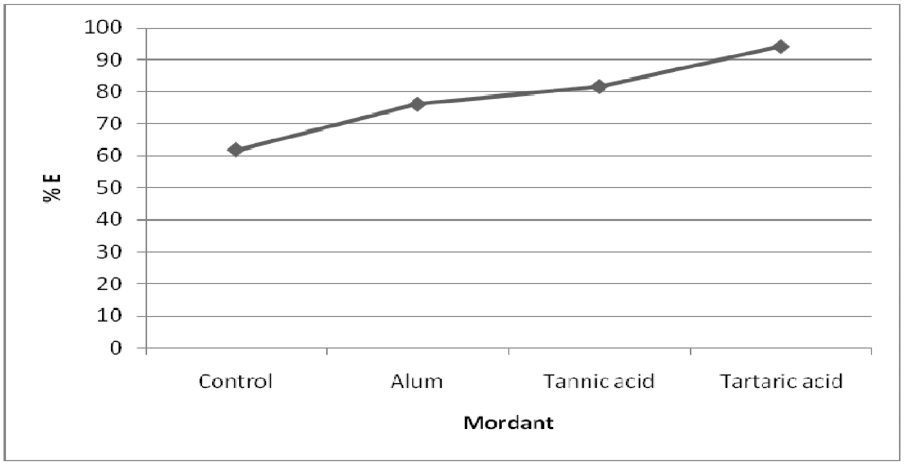


Figure 10
Effect of mordants on the total fixation efficiency (%T)

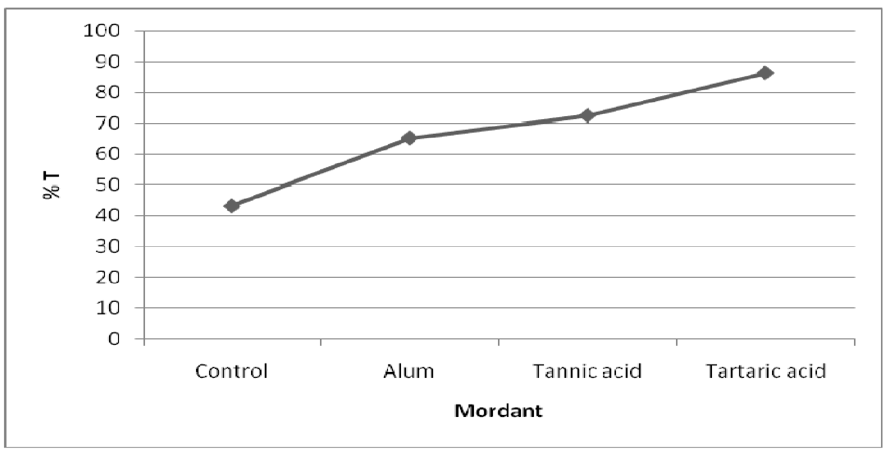


Figure 11
Effect of mordants on the fixation ratio (%F)

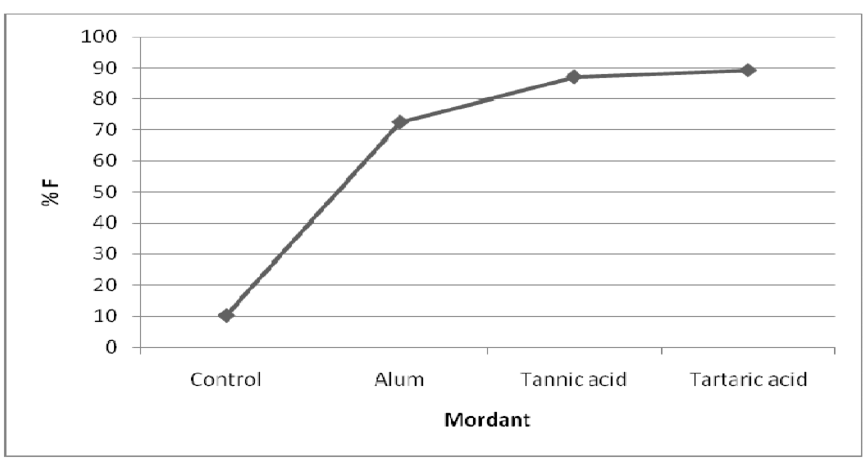
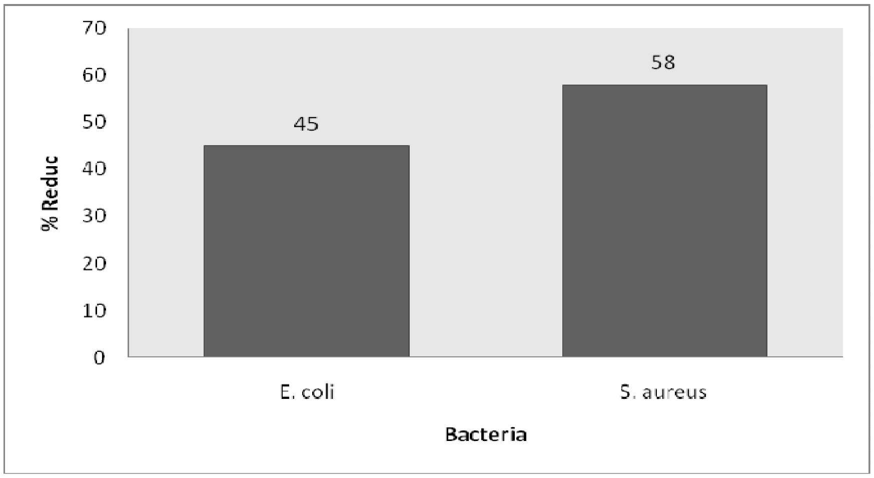


Figure 12
Antimicrobial activity of the dyed silk fabrics on E. coli and S. aureus



CONCLUSION

The natural colorant obtained from the *Casuarina equisetifolia* bark has been successfully used as an eco-friendly dye to obtain different shades of brown. Mordant treatment not only improved the color strength and fastness properties of this natural dye but also resulted in numerous shades. The use of this natural dye can therefore be a potential substitute for the synthetic dyes which contain harmful and banned components.

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